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(21) International Application Number: PCT/GB97/01141 (22) International Filing Date: 25 April 1997 (25.04.97) (30) Priority Data: 9608771.3 27 April 1996 (27.04.96) GB (71) Applicant (for all designated States except US): AGREVO UK LIMITED [GB/GB]; Hauxton, Cambridge CB2 5HU (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): STOCK, David [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB). BRIGGS, Geoffrey, Gower [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB). SIMPSON, Donald, James [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB). (74) Agent: WALDMAN, Ralph, David; AgrEvo UK Limited, Patent Dept., Chesterford Park, Saffron Walden, Essex CB10 1XL (GB).		(81) Designated States: AU, BG, BR, CA, CN, CZ, HU, IL, JP, KR, MX, NZ, PL, RO, RU, TR, UA, US, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FUNGICIDE SALTS (57) Abstract Combining pyrimethanil with an organic acid having a volatility of less than 2 Pa at 20 °C results in a product which has valuable physical and biological properties.		

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Fungicide salts

This invention relates to compounds having fungicidal activity.

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Pyrimethanil is a known fungicide, having the chemical name, 2-anilino-4,6-dimethylpyrimidine. However it has a relatively high vapour pressure which restricts its use. We have found that combining pyrimethanil with certain acids confers certain advantages to the compound.

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According to the invention there is provided a product obtained by combining pyrimethanil with an organic acid having a volatility of less than 2 Pa at 20°C.

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It is generally preferred that the acid is present in at least a stoichiometric amount and in this case a salt is formed between pyrimethanil and the acid. Excess acid may be an advantage, e.g. in a molar ratio of acid to pyrimethanil of up to 2:1.

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As stated above one advantage of the products of the invention in particular is that they have a reduced vapour pressure compared with the free pyrimethanil, which increases the persistence of the compound on the crop to be protected from fungal attack. The reduced volatility also reduces levels of fungicide in the atmosphere.

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In many cases the products have reduced phytotoxicity to certain plants.

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In some cases the salts have increased activity compared with the free pyrimethanil. Another advantage is that the products have physical and chemical properties which often make them amenable to provide better formulations than the free pyrimethanil. For example, the product of pyrimethanil with oleic acid is liquid which provides formulation advantages compared with the free pyrimethanil which is a solid.

Suitable organic acids with which the pyrimethanil can be combined are fatty acids, especially long chain fatty acids such as oleic acid and palmitic acid. Other

suitable organic acids include saccharin, sulfonic acids, such as camphorsulfonic acid, salicylic acid and jasmonic acid.

The products are useful in combating diseases for which pyrimethanil may be used e.g. *Botrytis* spp., especially *B. cinerea*, *Venturia* spp, *Altenaria* spp., and *Monolinia fructigena*. However the salt may also extend the useful activity to diseases such as mildews and particularly cereal powdery mildew (*Erysiphe graminis*) and glume blotch (*Leptosphaeria nodorum*).

10 The invention is illustrated in the following Examples.

Example 1

A solution of pyrimethanil (1.0 g), toluene (50 ml) and oleic acid (1.42 g) was allowed to stand overnight at room temperature. The toluene was evaporated under reduced pressure to give pyrimethanil oleate, as an oil. (compound 1)
nmr data:

CDCl₃ δ scale

	0.9	(3H , t , CH ₃)
20	1.25 - 1.42	(20H , m , 10 x CH ₂)
	1.62 - 1.76	(2H , m , CH ₂)
	1.95 - 2.1	(4H , m , 2 x CH ₂)
	2.34 - 2.42	(8H , m , 2xCH ₃ , CH ₂)
	5.3 - 5.42	(2H , m , CH = CH)
25	6.47	(1H , s , pyrimidine CH)
	7.0	(1H , t , ArH)
	7.32	(2H , t , ArH)
	7.72	(2H , d , ArH)
	8.67	(1H , br s , NH)

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Example 2

A solution of camphorsulfonic acid (1.25 g) in ethanol (10 ml) was added slowly to a solution of pyrimethanil (1 g) in toluene (20 ml) and the mixture allowed to stand for 30 minutes at room temperature. The mixture was evaporated under reduced pressure and the residue recrystallised from a mixture of diisopropyl ether

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and ethyl acetate to give pyrimethanil camphorsulfonate, m.p. 166-7°C.
(compound 2)

In a similar way there was obtained

- 5 a) pyrimethanil saccharinate, m.p. 164-5°C. (compound 3)
- b) pyrimethanil 7-trifluoromethylsaccharinate, m.p. 233-5°C. (compound 4)
- c) pyrimethanil 4,7-dimethoxysaccharinate, m.p. 187-8°C. (compound 5)
- d) pyrimethanil 4-chloro-7-methoxysaccharinate, m.p. 244-6°C.
(compound 6)
- 10 e) pyrimethanil p-toluenesulfonate, m.p. 200-2°C. (compound 7)
- f) pyrimethanil 2H-1-benzopyran-3-carboxylate, m.p. 126-7°C. (compound 8)
- g) pyrimethanil phenoxyacetate, m.p. 76-8°C. (compound 9)
- h) pyrimethanil phenylphosphonate, m.p. 126-8°C. (compound 10)
- i) dipyrimethanil malonate, m.p. 126-8°C. (compound 11)
- 15 j) dipyrimethanil phthalate, m.p. 144-6°C. (compound 12)
- k) pyrimethanil hydrogen phthalate, m.p. 149-51°C. (compound 13)

Example 3

This Example illustrates relative persistence of the products of the invention
20 compared with the free anilinopyrimidine.

Droplets (5 x 4 µl) of toluene solutions of radiolabelled pyrimethanil (0.05% w/v)
were applied to microscope cover slips (13 mm diameter), which were positioned
in Petri dishes. To some of the samples were added various fatty acids in molar
25 ratios of pyrimethanil to acid of 1:1 and 1:2. The Petri dishes were left in a
controlled environment room (20°C, 16 hours daylight) and after two days, slips
were removed to determine how much pyrimethanil remained. This was done by
transferring the slips to scintillation vials, each containing 10 ml of a dioxane
based scintillation cocktail and measuring the amount of radiation by liquid
30 scintillation counting. The results are as follows:

Table 1: Surface recovery of pyrimethanil after 2 days

Compound	Surface recovery (%)
Pyrimethanil + oleic acid (1:1 molar)	59.5
Pyrimethanil + oleic acid (1:2 molar)	77.9
Pyrimethanil + lauric acid (1:1 molar)	66.9
Pyrimethanil + lauric acid (1:2 molar)	80.1
Pyrimethanil + myristic acid (1:1 molar)	71.9
Pyrimethanil + myristic acid (1:2 molar)	63.3
Pyrimethanil + palmitic acid (1:1 molar)	61.6
Pyrimethanil + palmitic acid (1:2 molar)	71.5
Pyrimethanil	3.1

In a similar manner the example was repeated by adding saccharin to the pyrimethanil in the amounts shown (% w/v of the toluene solutions). Surface recovery measurements were made after 2 and 8 days

The results are as follows:

10 Table 2: Surface recovery of pyrimethanil after 2 days

Compound	Surface recovery (%)
Pyrimethanil + saccharin (0.05%)	57.9
Pyrimethanil (0.05%) + saccharin (0.1%)	90.3
Pyrimethanil (0.05%) + saccharin (0.2%)	95.8
Pyrimethanil (0.05%)	2.0

Table 3: Surface recovery of pyrimethanil after 8 days

Compound	Surface recovery (%)
Pyrimethanil (0.05%) + saccharin (0.05%)	43.6
Pyrimethanil (0.05%) + saccharin (0.1%)	80.0
Pyrimethanil (0.05%) + saccharin (0.2%)	94.0
Pyrimethanil (0.05%)	1.1

It will be seen that the addition of the various acids increases the persistence of
5 the pyrimethanil.

The compounds of Examples 1 and 2 also demonstrate greater levels of
persistence than the free pyrimethanil.

Example 4

5% Wettable powder formulations of compounds were diluted with water to the desired concentration and sprayed over wheat test plants. One day later the plants parts were inoculated with appropriate test pathogens and kept under controlled environment conditions suitable for maintaining plant growth and development of the disease. After an appropriate time, the degree of infection of the plant was visually estimated. Five replicates were used for each dose of test compound. The results are as follows. The rates of a.i. (active ingredient) in the tables are based on free pyrimethanil.

a) *Botrytis cinerea* (assessed 7 days after inoculation)

Compound No	% Control of disease at	
	5 g ai/hl	2 g ai/hl
5	94.4	85.4
6	94.4	88.7
7	91.0	83.1
8	93.2	84.2
9	90.4	75.2
10	94.4	87.6
12	91.0	77.5
pyrimethanil (5% WP)	85.4	75.2
SCALA	78.6	55.0

SCALA is the commercial 40% SC formulation of pyrimethanil

b) *Erysiphe graminis f. sp. tritici* (assessed 7 days after inoculation)

Compound No	% Control of disease at	
	100g ai/ha	25g ai/ha
4	39.7	15.5
8	75.9	27.6
12	51.7	3.4
pyrimethanil (5% WP)	27.6	3.4
SCALA	0	15.5

c) *Leptosphaeria nodorum* (assessed 21 days after inoculation)

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Compound No	% Control of disease at	
	100g ai/ha	25g ai/ha
5	32.8	15.2
7	22.2	15.2
8	36.4	25.8
12	39.9	15.2
pyrimethanil (5% WP)	11.6	1.0
SCALA	15.2	11.6

Claims

1. A product obtained by combining pyrimethanil with an organic acid having a volatility of less than 2 Pa at 20°C.
- 5 2. A fungicidal composition which comprises a product as claimed in claim 1 in admixture with an agriculturally acceptable diluent or carrier.
3. A method of combating phytopathogenic fungi, at a locus infested or liable
10 to be infested therewith, which comprises applying to the locus a compound of a product as claimed in claim 1.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/GB 97/01141

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N43/54 //(A01N43/54,41:04,37:10,37:06,37:04,37:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	AGRONOMIE, vol. 14, 1994, pages 541-554, XP002039434 P. LEROUX: "Influence du pH, d'acides aminés et de diversss substnces organiques sur la fongitoxicité du pyriméthanyl (....) vis-à-vis de certaines souches de Botrytis cinerea. " see page 544, column 1, paragraph 2 - page 550, column 1, paragraph 1	1-3
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A	EP 0 642 735 A (BASF AG) 15 March 1995 see page 3, line 56 - page 4, line 12 -/--	1-3



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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